

## VERIFICATION OF TRANSLATION

Re : Japanese Patent Application No. 2002-382311

I, Mihoko KAWAKAMI, of c/o Hosoda International Patent Office, OMM Building 5th Floor, P.O. Box 26, 1-7-31 Otemae, Chuo-ku, Osaka 540-6591, JAPAN, hereby declare that I am the translator of the documents attached and certify that the following is a true translation of the best of my knowledge and belief.

Dated this 21st day of December, 2005

  
Mihoko KAWAKAMI

**JAPAN PATENT OFFICE**

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[Document] Specification

[Title of the Invention] Water-based Ink

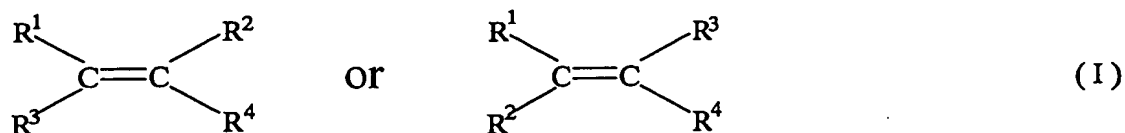
[Claims]

[Claim 1] A water-based ink comprising an aqueous dispersion of polymer particles of a water-dispersible polymer having an alkyl group of at least 13 carbon atoms in its side chain, and a hydrophobic dye.

[Claim 2] The water-based ink according to claim 1, wherein the hydrophobic dye is at least one dye selected from the group consisting of a copper phthalocyanine dye, a quinophthalone dye and a xanthene dye.

[Claim 3] The water-based ink according to claim 1 or 2, wherein the water-dispersible polymer is a vinyl polymer prepared by copolymerizing a monomer composition comprising a monomer represented by Formula (I):

[Ka 1]



wherein each of  $\text{R}^1$  and  $\text{R}^2$  is independently hydrogen atom or methyl group;  $\text{R}^3$  is hydrogen atom, carboxyl group, a  $\text{COOR}^5$  group wherein  $\text{R}^5$  is an alkyl group having at least 13 carbon atoms or a  $\text{CONR}^5\text{R}^6$  group wherein  $\text{R}^5$  is as defined above and  $\text{R}^6$  is hydrogen atom, an alkyl group or an aryl group;  $\text{R}^4$  is a  $\text{COOR}^5$  group wherein  $\text{R}^5$  is as defined above, or a  $\text{CONR}^5\text{R}^6$  group wherein  $\text{R}^5$  and  $\text{R}^6$  are as defined above,

a salt-forming group-containing monomer, and a monomer copolymerizable with the monomer represented by the Formula (I) and the salt-forming group-containing monomer.

[Claim 4] The water-based ink according to any one of claims 1 to 3, wherein the water-dispersible polymer has an anionic salt-forming group and an acid value of 30 to 120 mg KOH/g.

[Claim 5] The water-based ink according to any one of claims 1 to 4, wherein the alkyl group in the side chain of the water-dispersible polymer is linear.

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains]

The present invention relates to a water-based ink. More specifically, the present invention relates to a water-based ink which can be suitably used as an ink for inkjet recording, and the like.

[0002]

[Prior Art]

A water-based ink containing an aqueous dispersion of polymer particles containing a hydrophobic dye (hereinafter referred to as "dispersion of a dye-containing polymer") has some characteristics such as water resistance and bleeding resistance which are characteristics of the dispersion of a dye-containing polymer, and vividness, good color reproducibility and high optical density which are characteristics of the dye-based ink. As an example of a water-based ink in which the dispersion of a dye-containing polymer as described above is used, there have been known a colorant in which a vinyl polymer is impregnated with a hydrophobic dye (see, for example, Patent Document 1); a dispersion of a dye-containing polymer, in which a water-dispersible polyester is impregnated with a water-insoluble dye (see, for example,

Patent Document 2); and a dispersion of a dye-containing polymer, in which a grafted resin is used as a water-dispersible polymer (see, for example, Patent Documents 3 to 5).

[0003]

However, in a water-based ink, in particular, a water-based ink for use in inkjet recording, a water-soluble organic solvent for controlling the permeability of ink to paper (hereinafter referred to as permeability controlling solvent), a surfactant and the like are added as well as a dispersion of a dye-containing polymer. As the permeability controlling solvent, generally, a glycol ether, 2-pyrrolidone, isopropanol and the like have been used. However, these solvents dissolve the water-dispersible polymer. Therefore, the resin is dissolved and swelled when an ink is formulated with these solvents. As a result, the aqueous dispersion is degraded, which results in problems of increase in the viscosity of ink, increase in the particle diameter of dispersion, and even sedimentation of the polymer due to aggregation in the worst case.

[0004]

Also, in the conventional dispersions of a dye-containing polymer, when an ink is formulated with the solvent as described above, the hydrophobic dye incorporated in the dispersed resin is dissolved in the solvent and extracted to the liquid phase. Therefore, the conventional inks have a problem that the dye is separated out when they are stored for a long period of time. As for the surfactant, when a nonionic surfactant having a low HLB is used, such nonionic surfactant causes degradation of the dispersion as in the above case, and the same problems arise.

[0005]

Therefore, in order to solve these problems, it has been considered to use an additive including a water-soluble organic solvent which is less likely to have an adverse effect on a dispersion of a dye-containing polymer, such as a polyhydric alcohol, or a surfactant such as a nonionic surfactant having a high HLB or an ionic surfactant. However, when such an additive is added in a large amount, there are defects such as occurrence of bleeding and decrease in optical density. Accordingly, it can be considered to reduce the amount of a dye to be contained in the dispersion of a dye-containing polymer. In this case, there is a defect that optical density and color reproducibility are lowered.

[0006]

[Patent Document 1]

Japanese Patent Laid-Open No. 54-058504

[Patent Document 2]

Japanese Patent Laid-Open No. 07-34023

[Patent Document 3]

Japanese Patent Laid-Open No. 08-035081

[Patent Document 4]

Japanese Patent Laid-Open No. 08-048498

[Patent Document 5]

Japanese Patent Laid-Open No. 09-024680

[0007]

[Problems to Be Solved by the Invention]

An object of the present invention is to provide a water-based ink which is excellent in storage stability and color tone, and exhibits high optical density and provides a printout having excellent rubbing resistance. In addition, an object of

the present invention is to provide a water-based ink which is excellent in printing reliability in addition to the above-mentioned properties when used for inkjet recording.

[0008]

[Means to Solve the Problems]

The present invention relates to a water-based ink comprising an aqueous dispersion of polymer particles of a water-dispersible polymer having an alkyl group of at least 13 carbon atoms in its side chain (hereinafter referred to as "aqueous dispersion of dye-containing polymer particles"), and a hydrophobic dye.

[0009]

[Modes for Carrying out the Invention]

The water-based ink of the present invention contains an aqueous dispersion of polymer particles of a water-dispersible polymer, and a hydrophobic dye. One of the major characteristics of the water-based ink of the present invention resides in that the water-dispersible polymer has an alkyl group of at least 13 carbon atoms in its side chain.

[0010]

The hydrophobic dye is (1) contained in polymer particles of a water-dispersible polymer having an alkyl group of at least 13 carbon atoms in its side chain (hereinafter simply referred to as "water-dispersible polymer"), and the polymer particles are contained in the water-based ink in the form of an aqueous dispersion. Alternatively, (2) the hydrophobic dye is dispersed in water with a surfactant or a water-soluble polymer, to form an aqueous dispersion of the hydrophobic dye, and the aqueous dispersion is contained in the water-based ink



together with an aqueous dispersion of polymer particles of a water-dispersible polymer.

[0011]

The surfactant used when dispersing a pigment with a surfactant includes anionic surfactants, cationic surfactants, nonionic surfactants or amphoteric surfactants. Among them, a sodium salt of  $\beta$ -naphthalenesulfonate-formaldehyde condensate (for instance, trade names: Demol N, Demol RN, Demol MS and the like commercially available from Kao Corporation), and carboxylate polymer surfactants (for instance, trade names: Poise 520, Poise 521, Poise 530 and the like commercially available from Kao Corporation) are preferable.

[0012]

It is desired that the amount of the surfactant is 1 to 120 parts by weight, preferably 3 to 70 parts by weight, more preferably 5 to 30 parts by weight, based on 100 parts by weight of the pigment, from the viewpoint of dispersion stability of the colorant in the ink and jetting property of the ink.

[0013]

The water-soluble polymer used for dispersing a pigment in water includes water-soluble vinyl polymers, water-soluble ester polymers, water-soluble urethane polymers and the like. Among them, the water-soluble vinyl polymers are preferable.

[0014]

The "water-soluble polymer" as used herein refers to a polymer which has a solubility of at least 1 g in 100 g of water at 25°C after neutralization.

[0015]

Since the water-dispersible polymer as described above is used in the water-based ink of the present invention, a colorant having stabilized physical properties can be obtained even when various organic solvents are added, so that optical density, bleeding resistance and feathering are improved, thereby exhibiting high optical density.

[0016]

The number of carbon atoms of alkyl group in the side chain of the water-dispersible polymer is at least 13, preferably at least 18, more preferably at least 22, from the viewpoint of storage stability for the ink formulation. Also, the aqueous dispersion contains a polymer prepared by polymerizing a monomer composition containing a monomer having an alkyl group of at least 13 carbon atoms and a monomer copolymerizable with this alkyl group-containing monomer. Therefore, the number of carbon atoms of the alkyl group in the side chain is preferably at most 30, more preferably at most 28, still more preferably at most 26, from the viewpoint of promoting the polymerization with a copolymerizable monomer or the conversion into an alkyl side chain having at least 13 carbon atoms. From such viewpoint, the number of carbon atoms of the alkyl group in the side chain of the water-dispersible polymer is at least 13, preferably 13 to 30, more preferably 14 to 28, still more preferably 16 to 22.

[0017]

The alkyl group in the side chain which the water-dispersible polymer may be either linear or branched. The alkyl group is preferably linear from the viewpoint of storage stability for the ink formulation.

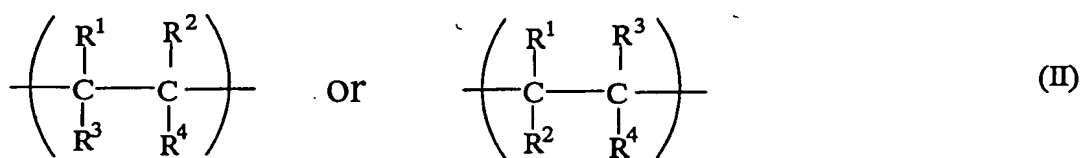
[0018]

Representative examples of a preferred water-dispersible polymer include

a polymer having a recurring structure [hereinafter referred to as recurring structure (I)] represented by the formula (II):

[0019]

[Ka 2]



[0020]

wherein each of  $\text{R}^1$  and  $\text{R}^2$  is independently hydrogen atom or methyl group;  $\text{R}^3$  is hydrogen atom, carboxyl group, a  $\text{COOR}^5$  group wherein  $\text{R}^5$  is an alkyl group having at least 13 carbon atoms or a  $\text{CONR}^5\text{R}^6$  group wherein  $\text{R}^5$  is as defined above and  $\text{R}^6$  is hydrogen atom, an alkyl group or an aryl group;  $\text{R}^4$  is a  $\text{COOR}^5$  group wherein  $\text{R}^5$  is as defined above, or a  $\text{CONR}^5\text{R}^6$  group wherein  $\text{R}^5$  and  $\text{R}^6$  are as defined above, and

a recurring structure having a salt-forming group.

[0021]

$\text{R}^4$  is a  $\text{COOR}^5$  group or a  $\text{CONR}^5\text{R}^6$  group. Since  $\text{R}^5$  constitutes the alkyl group in the side chain,  $\text{R}^5$  is an alkyl group having at least 13 carbon atoms, preferably an alkyl group having 13 to 30 carbon atoms, more preferably an alkyl group having 18 to 26 carbon atoms.

[0022]

$\text{R}^6$  is hydrogen atom, an alkyl group or an aryl group. Among the alkyl groups, an alkyl group having 1 to 30 carbon atoms is preferable, and an alkyl group having 1 to 26 carbon atoms is more preferable. Also, among the aryl groups, an aryl group having 6 to 12 carbon atoms is preferable, and an aryl

group having 6 to 8 carbon atoms is more preferable.

[0023]

The water-dispersible polymer can be prepared by, for instance,

1. a process which comprises polymerizing a monomer composition containing (A) a monomer which is formed into the recurring structure (I) after polymerization [hereinafter referred to as "monomer (I)"], (B) a salt-forming group-containing monomer which is formed into the recurring structure having the salt-forming group after polymerization, and (C) a monomer copolymerizable with (A) the monomer (I) and (B) the salt-forming group-containing monomer (hereinafter referred to as "copolymerizable monomer") (hereinafter referred to as "preparation process 1"); and

[0024]

2. a process which comprises polymerizing a monochlor composition containing (A) a functional group-containing monomer [hereinafter referred to as "monomer (I) P"] which is formed into the recurring structure (I) after reaction, (B) the salt-forming group-containing monomer and (C) a monomer copolymerizable with the monomer (I) P and the salt-forming group-containing monomer [hereinafter referred to as "monomer copolymerizable with the monomer (I) P and the like"], and/or an acid anhydride, and thereafter carrying out a reaction to form the recurring structure (I) and, if necessary, carrying out a reaction to form the recurring structure having the salt-forming group (hereinafter referred to as "preparation process 2").

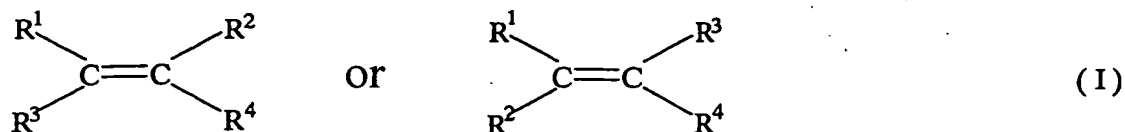
[0025]

Representative examples of a preferred water-dispersible polymer include a vinyl polymer prepared by copolymerizing a monomer composition containing

a monomer represented by the formula (I):

[0026]

[Ka 3]



[0027]

wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are as defined above [hereinafter referred to as monomer (I)],

a salt-forming group-containing monomer, and a monomer copolymerizable with the monomer (I) and the salt-forming group-containing monomer.

[0028]

As concrete examples of the monomer (I), stearyl methacrylate, behenyl methacrylate, stearyl acrylate, behenyl acrylate, stearyl maleate, distearyl maleate, monobehenyl maleate and dibehenyl maleate are preferable. These monomers can be used alone or in admixture of at least two kinds. Among these monomers, behenyl methacrylate and behenyl acrylate are more preferable from the viewpoint of storage stability for the ink formulation and copolymerization ability.

[0029]

The salt-forming group-containing monomer includes unsaturated carboxylic acid monomers, unsaturated sulfonic acid monomers, unsaturated phosphoric acid monomers and the like. Specifically, the unsaturated carboxylic acid monomers include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, citraconic acid, 2-methacryloyloxymethyl

succinic acid, their anhydrides and salts. The unsaturated sulfonic acid monomers include styrenesulfonic acid, 2-acrylamide-2-methylpropanesulfonic acid, 3-sulfopropene (meth)acrylate, bis(3-sulfopropyl) itaconate, their salts and the like; as well as sulfonic acid monoester of 2-hydroxyethyl (meth)acrylic acid, and salts thereof. The unsaturated phosphoric acid monomers include vinylphosphonic acid, vinyl phosphate, bis(methacryloyloxyethyl) phosphate, diphenyl-2-methacryloyloxyethyl phosphate, dibutyl-2-acryloyloxyethyl phosphate, dioctyl-2-(meth)acryloyloxyethyl phosphate and the like. These salt-forming group-containing monomers can be used alone or in admixture of at least two kinds. Among these salt-forming group-containing monomers, the unsaturated carboxylic acid monomers having an anionic salt-forming group, such as methacrylic acid and acrylic acid, are preferable from the viewpoint of copolymerization ability and storage stability.

[0030]

The above-mentioned copolymerizable monomer include, for instance, (meth)acrylates having an alkyl group of 1 to 12 carbon atoms, such as methyl (meth)acrylate, ethyl (meth)acrylate, (iso)propyl (meth)acrylate, (iso or tertiary)butyl (meth)acrylate, (iso)amyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, (iso)octyl (meth)acrylate, (iso)decyl (meth)acrylate, (iso)dodecyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate and 3-hydroxypropyl (meth)acrylate; and styrenic monomers such as styrene, vinyltoluene, 2-methylstyrene and chlorostyrene; and the like. These monomers can be used alone or in admixture of at least two kinds.

[0031]

Incidentally, the above-mentioned “(iso or tertiary)” and “(iso)” mean both of the case where these groups are present and the case where these groups are absent. When these groups are absent, the monomer is in the form of normal.

[0032]

The monomer (I) P includes halogenated (meth)acrylates. The monomer (I) P is reacted with an alcohol or an amine after the polymerization, to be formed into a recurring structure derived from the (meth)acrylate or a recurring structure derived from the (meth)acrylic acid amide.

[0033]

In the preparation process 1, it is desired that the amount of the monomer (I) is 20 to 80 parts by weight, preferably 30 to 70 parts by weight, that the amount of the salt-forming group-containing monomer is 2 to 20 parts by weight, preferably 5 to 15 parts by weight, and that the amount of the copolymerizable monomer is 5 to 78 parts by weight, preferably 15 to 65 parts by weight, based on the total amount 100 parts by weight of the monomer (I), the salt-forming group containing monomer and the copolymerizable monomer, from the viewpoint of copolymerization ability, storage stability and mixing stability for the components of the ink.

[0034]

In the preparation process 2, the amount of the monomers are such that the amount of the monomer (I) in the preparation process 1 is substituted to the amount of the monomer (I) P in the preparation process 2, the amount of the salt-forming group-containing monomer in the preparation process 1 is substituted to the amount of the salt-forming group-containing monomer in the preparation

process 2, and the amount of the copolymerizable monomer in the preparation process 1 is substituted to the amount of the monomer copolymerizable with the monomer (I) P and the like in the preparation process 2.

[0035]

The water-dispersible polymer can be prepared, for instance, by the following processes:

**Preparation Process 1:**

- i) a process for copolymerizing a monomer composition containing a (meth)acrylate having an alkyl group of at least 13 carbon atoms or (meth)acrylic amide;
- ii) a process for copolymerizing a monomer composition containing a maleate having an alkyl group of at least 13 carbon atoms or maleic amide;
- iii) a process for reacting an aliphatic alcohol having at least 13 carbon atoms or a primary or secondary amine having an alkyl group of at least 13 carbon atoms with a halogenated (meth)acrylate or maleic anhydride, and thereafter copolymerizing a monomer composition containing the reaction product obtained;
- iv) a process for reacting a monomer having an epoxy group, such as glycidyl (meth)acrylate, with a fatty acid having an alkyl group of at least 13 carbon atoms, and thereafter copolymerizing a monomer composition containing the reaction product obtained.

**Preparation Process 2:**

- v) a process for copolymerizing a monomer composition containing a halogenated (meth)acrylate or maleic anhydride, and thereafter reacting the resulting polymer with an aliphatic alcohol having at least 13 carbon atoms or a



primary or secondary amine having an alkyl group of at least 13 carbon atoms.

[0036]

The water-dispersible polymer can be obtained by polymerizing the above-mentioned monomer composition by a known polymerization method such as a bulk polymerization method, a solution polymerization method, a suspension polymerization method or an emulsion polymerization method.

[0037]

Among these polymerization methods, the solution polymerization method is preferable. The solvent used for the solution polymerization method include aliphatic alcohols such as ethanol and propanol; ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone; esters such as ethyl acetate; aromatic solvents such as benzene and toluene; and the like. These organic solvents can be used alone or in admixture of at least two kinds.

[0038]

In the polymerization, a polymerization initiator is usually used. As the polymerization initiator, for instance, azo compounds such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), dimethyl-2,2'-azobisbutyrate, 2,2'-azobis(2-methylbutyronitrile) and 1,1'-azobis(1-cyclohexanecarbonitrile) are preferable. Also, the polymerization initiator includes a radical polymerization initiator such as organic peroxides such as t-butyl peroxyoctoate, dicumyl peroxide, di-t-butyl peroxide and dibenzoyl oxide.

[0039]

It is desired that the amount of the polymerization initiator is 0.001 to 2.0% by weight, preferably 0.01 to 1.5% by weight, of the total amount of the

monomers.

[0040]

Incidentally, in the polymerization, a polymerization chain transfer agent can be used. Concrete examples of the polymerization chain transfer agent include, for instance, mercaptans such as octyl mercaptan, n-dodecyl mercaptan, t-dodecyl mercaptan, n-hexadecyl mercaptan, n-tetradecyl mercaptan and t-tetradecyl mercaptan; xanthogenndisulfides such as dimethyl xanthogenndisulfide, diethyl xanthogenndisulfide and diisopropyl xanthogenndisulfide; thiuram disulfides such as tetramethyl thiuram disulfide, tetraethyl thiuram disulfide and tetrabutyl thiuram disulfide; halogenated hydrocarbons such as carbon tetrachloride and ethylene bromide; hydrocarbons such as pentaphenylethane; unsaturated cyclic hydrocarbon compounds such as acrolein, methacrolein, allyl alcohol, 2-ethylhexyl thioglycolate, terpinolene,  $\alpha$ -terpinene,  $\gamma$ -terpinene, diterpene,  $\alpha$ -methylstyrene dimer (preferably those containing at least 50% by weight of 2,4-diphenyl-4-methyl-1-pentene), 9,10-dihydroanthracene, 1,4-dihydronaphthalene, indene and 1,4-cyclohexadiene; unsaturated heterocyclic compounds such as xanthene and 2,5-dihydrofuran; and the like. These polymerization chain transfer agents can be used alone or in admixture of at least two kinds.

[0041]

The polymerization conditions cannot be absolutely determined because the conditions differ depending upon the type of the radical polymerization initiator, the monomers and the solvent, and the like. Usually, the polymerization temperature is preferably 30° to 100°C, more preferably 50° to 80°C, and the polymerization time is 1 to 10 hours or so.

[0042]

Incidentally, it is preferable that the atmosphere for polymerization is an atmosphere of an inert gas such as nitrogen.

[0043]

After the termination of the polymerization reaction, the formed polymer can be isolated from the reaction solution by a known method such as re-precipitation or removal of a solvent. Also, the resulting polymer can be purified to remove unreacted monomers and the like by the repeat of re-precipitation, membrane separation, a chromatographic method, an extraction method or the like.

[0044]

The weight-average molecular weight of the polymer thus obtained is preferably 3000 to 80000, more preferably 3000 to 50000, from the viewpoint of avoiding scorching on the printer head, improving the durability of the ink after printing and facilitating the formation of the dispersion.

[0045]

In addition, it is preferable that the water-dispersible polymer has an anionic salt-forming group and an acid value of 30 to 120 mg KOH/g from the viewpoint of storage stability and jetting stability.

[0046]

Examples of the hydrophobic dye include oil-soluble dyes, disperse dyes and the like. The solubility at 20°C of the hydrophobic dye in an organic solvent which is used for dissolving the hydrophobic dye when preparing an aqueous dispersion is preferably at least 2 g/L, more preferably 20 to 500 g/L.

[0047]

The kind of the oil-soluble dyes is not limited to the specified ones.

Preferable oil-soluble dyes include, for instance, black dyes such as C.I. Solvent Black 3, 7, 27, 29 and 34, Nigrosine black dyes; C.I. Solvent Yellow 14, 16, 19, 29, 30, 56, 82, 93 and 162; C.I. Solvent Red 1, 3, 8, 18, 24, 27, 43, 49, 51, 72, 73, 109, 122, 132 and 218; C.I. Solvent Violet 3; C.I. Solvent Blue 2, 11, 25, 35 and 70; C.I. Solvent Green 3 and 7; C.I. Solvent Orange 2; and the like. More preferable oil-soluble dyes include C.I. Solvent Yellow 29 and 30 for yellow, C.I. Solvent Blue 70 for cyan, C.I. Solvent Red 18 and 49 for magenta, and C.I. Solvent Black 3 and Nigrosine black dyes for black.

[0048]

Commercially available oil-soluble dyes include, for instance, Nubian Black PC-0850, Oil Black HBB, Oil Black 860, Oil Yellow 129, Oil Yellow 105, Oil Pink 312, Oil Red 5B, Oil Scarlet 308, Vali Fast Blue 2606, Oil Blue BOS [hereinabove commercially available from Orient Chemical Co., Ltd.]; Neopen Yellow 075, Neopen Mazenta SE1378, Neopen Blue 807, Neopen Blue FF4012, Neopen Cyan FF4238 [hereinabove commercially available from BASF]; and the like.

[0049]

The disperse dye used in the present invention are not limited to those listed below. Concrete examples of particularly preferred disperse dye include, for instance, C.I. Disperse Yellow 5, 42, 54, 64, 79, 82, 83, 93, 99, 100, 119, 122, 124, 126, 160, 184:1, 186, 198, 199, 201, 204, 224 and 237; C.I. Disperse Orange 13, 29, 31:1, 33, 49, 54, 55, 66, 73, 118, 119 and 163; C.I. Disperse Red 54, 60, 72, 73, 86, 88, 91, 93, 111, 126, 127, 134, 135, 143, 145, 152, 153, 154, 159, 164, 167:1, 177, 181, 204, 206, 207, 221, 239, 240, 258, 277, 278, 283, 311,

323, 343, 348, 356 and 362; C.I. Disperse Violet 33; C.I. Disperse Blue 56, 60, 73, 87, 113, 128, 143, 148, 154, 158, 165, 165:1, 165:2, 176, 183, 185, 197, 198, 201, 214, 224, 225, 257, 266, 267, 287, 354, 358, 365 and 368; C.I. Disperse Green 6:1 and 9; and the like.

[0050]

The aqueous dispersion of the dye-containing polymer particles can be prepared by a generally known method for preparing a resin emulsion, such as a forced emulsion method, a phase inversion emulsion method, an emulsion polymerization method or a suspension polymerization method.

[0051]

The aqueous dispersion of polymer particles containing a hydrophobic dye can be prepared by a known emulsion method. The aqueous dispersion can be obtained, for instance, by dissolving a water-insoluble polymer and a hydrophobic dye in an organic solvent, adding a neutralizing agent to the resulting solution as occasion demands, to ionize a salt-forming group of the water-insoluble polymer, adding water thereto, thereafter dispersing the resulting solution using a dispersing apparatus or an ultrasonic emulsifier as occasion demands, and distilling off the organic solvent to phase-invert to a water-based system.

[0052]

The emulsifier includes a common ultrasonic emulsifier, an ultra high pressure homogenizer, a membrane emulsifier and the like. Among them, the emulsifier includes Microfluidizer (commercially available from Microfluidizer, trade name), Nanomizer (commercially available from Tokushu Kika Kogyo Co. Ltd., trade name), an ultrasonic homogenizer (commercially available from

NIPPON SEIKI SEISAKUSHO) and the like.

[0053]

The minimum filmforming temperature of the aqueous dispersion of the dye-containing polymer particles is not limited to specified ones, and it is desired that the temperature is preferably at least 10°C.

[0054]

The water-based ink is obtained by mixing the aqueous dispersion of the dye-containing polymer particles, a permeability controlling solvent, a surfactant and a moisturizing agent, and filtering the resulting mixture as occasion demands.

[0055]

[Examples]

#### Example 1

##### (1) Synthesis of Vinyl Polymer

Nitrogen gas replacement was sufficiently carried out in a 500-mL separable flask equipped with a dropping funnel and a Dimroth condenser. Thereafter, the flask was charged with 30 g of tridecyl methacrylate, 2 g of acrylic acid, 8 g of methoxypolyethylene glycol #230 methacrylate, 0.4 g of 2-mercaptoethanol and 10 g of 2-butanone, and the temperature of the ingredients was raised to 60°C under reflux. The dropping funnel was charged with 120 g of tridecyl methacrylate, 8 g of acrylic acid, 32 g of methoxypolyethylene glycol #230 methacrylate, 1.6 g of 2-mercaptoethanol, 1.6 g of 2,2'-azobis(2,4-dimethylvaleronitrile) and 40 g of 2-butanone, and the resulting mixture was added dropwise to the flask over a period of 3 hours. After the dropwise addition, the resulting mixture was aged for 2 hours, and 0.4 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was added thereto. The resulting mixture

was aged for additional 2 hours, and thereafter 150 g of 2-butanone was added thereto.

A solution of a vinyl polymer having a weight-average molecular weight of 6500 was thus prepared.

[0056]

(2) Aqueous Dispersion of Dye-Containing Polymer Particles

The amount 2.5 g of a magenta dye (commercially available from Orient Chemical Co., Ltd., trade name: Oil Pink 312) was dissolved in 25 g of toluene. To the solution was added 5.0 g of the polymer solution obtained in the above (1), and the resulting solution was sufficiently stirred to dissolve the polymer. After the dissolution was confirmed, 1.74 g of 1 N aqueous potassium hydroxide and 125 g of purified water were added, and the resulting solution was further sufficiently stirred.

[0057]

After stirring, the solution was subjected to emulsification for 20 minutes with an ultrasonic homogenizer at 400  $\mu$ A. Thereafter, toluene was removed by heating under reduced pressure. Finally, the resulting emulsion was filtered through a filter having a pore size of 0.8  $\mu$ m, to prepare an aqueous dispersion of the dye-containing polymer particles in which the dye was incorporated in the vinyl polymer.

[0058]

Preparation Example 2

(1) Synthesis of Vinyl Polymer

Nitrogen gas replacement was sufficiently carried out in a 500-mL separable flask equipped with a dropping funnel and a Dimroth condenser.

Thereafter, the flask was charged with 20 g of behenyl methacrylate, 4 g of methacrylic acid, 16 g of methyl methacrylate, 0.4 g of 2-mercaptoethanol and 10 g of 2-butanone, and the temperature of the ingredients was raised to 60°C under reflux. The dropping funnel was charged with 80 g of behenyl methacrylate, 16 g of methacrylic acid, 64 g of methyl methacrylate, 1.6 g of 2-mercaptoethanol, 1.6 g of 2,2'-azobis(2,4-dimethylvaleronitrile) and 40 g of 2-butanone, and the resulting mixture was added dropwise to the flask over a period of 3 hours. After the dropwise addition, the resulting mixture was aged for 2 hours, and 0.4 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was added thereto. The resulting mixture was aged for additional 2 hours, and thereafter 150 g of 2-butanone was added thereto. A solution of a vinyl polymer having a weight-average molecular weight of 6000 was thus obtained.

[0059]

(2) Aqueous Dispersion of Dye-Containing Polymer Particles

The amount 2.5 g of a cyan dye (commercially available from BASF, Neozapon Blue 807) was dissolved in 25 g of toluene. To the solution was added 5.0 g of the polymer solution obtained in the above (1), and the resulting solution was sufficiently stirred to dissolve the polymer. After the dissolution was confirmed, 1.45 g of 1 N aqueous potassium hydroxide and 125 g of purified water were added, and the resulting solution was further sufficiently stirred. After stirring, the solution was subjected to emulsification for 20 minutes with an ultrasonic homogenizer at 400  $\mu$ A. Thereafter, toluene was removed by heating under reduced pressure. Finally, the resulting emulsion was filtered through a filter having a pore size of 0.8  $\mu$ m, to give an aqueous dispersion of the dye-containing polymer particles.



[0060]

Preparation Example 3

(1) Synthesis of Vinyl Polymer

Nitrogen gas replacement was sufficiently carried out in a 500-mL separable flask equipped with a dropping funnel and a Dimroth condenser. Thereafter, the flask was charged with 30 g of styrene, 2 g of maleic anhydride, 8 g of ethyl methacrylate, 0.4 g of 2-mercaptoethanol and 10 g of 2-butanone, and the temperature of the ingredients was raised to 60°C under reflux. The dropping funnel was charged with 120 g of styrene, 8 g of maleic anhydride, 32 g of ethyl methacrylate, 1.6 g of 2-mercaptoethanol, 1.6 g of 2,2'-azobis(2,4-dimethylvaleronitrile) and 40 g of 2-butanone, and the resulting mixture was added dropwise to the flask over a period of 3 hours. After the dropwise addition, the resulting mixture was aged for 2 hours, and 0.4 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was added thereto. The resulting mixture was aged for additional 2 hours, and thereafter 27 g of tridecyl alcohol and 0.09 g of triethylamine were added thereto, and the resulting mixture was aged for 3 hours. Thereafter, 150 g of 2-butanone was added, to prepare a solution of a vinyl polymer having a weight-average molecular weight of 7200.

[0061]

(2) Aqueous Dispersion of Dye-Containing Polymer Particles

The amount 2.5 g of a yellow dye (commercially available from Arimoto Kagaku K. K., Oil Yellow 129) was dissolved in 25 g of toluene. To the solution was added 5.0 g of the polymer solution obtained in the above (1), and the resulting solution was sufficiently stirred to dissolve the polymer. After the dissolution was confirmed, 1.63 g of 1 N aqueous potassium hydroxide and 125

g of purified water were added, and the resulting solution was further sufficiently stirred. After stirring, the solution was subjected to emulsification for 20 minutes with an ultrasonic homogenizer at 400  $\mu$ A. Thereafter, toluene was removed by heating under reduced pressure. Finally, the resulting emulsion was filtered through a filter having a pore size of 0.8  $\mu$ m, to give an aqueous dispersion of the dye-containing polymer particles.

[0062]

#### Preparation Example 4

##### (1) Synthesis of Vinyl Polymer

Nitrogen gas replacement was sufficiently carried out in a 500-mL separable flask equipped with a dropping funnel and a Dimroth condenser. Thereafter, the flask was charged with 30 g of stearyl methacrylate, 2 g of methacrylic acid, 8 g of 2-hydroxyethyl methacrylate, 0.4 g of 2-mercaptoethanol and 10 g of 2-butanone, and the temperature of the ingredients was raised to 60°C under reflux. The dropping funnel was charged with 120 g of stearyl methacrylate, 8 g of methacrylic acid, 32 g of 2-hydroxyethyl methacrylate, 1.6 g of 2-mercaptoethanol, 1.6 g of 2,2'-azobis(2,4-dimethylvaleronitrile) and 40 g of 2-butanone, and the resulting mixture was added dropwise to the flask over a period of 3 hours. After the dropwise addition, the resulting mixture was aged for 2 hours, and 0.4 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was added thereto. The resulting mixture was aged for additional 2 hours, and thereafter 150 g of 2-butanone was added thereto. A solution of a vinyl polymer having a weight-average molecular weight of 6900 was thus prepared.

[0063]

## (2) Aqueous Dispersion of Dye-Containing Polymer Particles

The amount 2.5 g of a magenta dye (commercially available from BASF, Neopen Magenta 525) was dissolved in 25 g of toluene. To the solution was added 5.0 g of the polymer solution obtained in the above (1), and the resulting solution was sufficiently stirred to dissolve the polymer. After the dissolution was confirmed, 1.45 g of 1 N aqueous sodium hydroxide and 125 g of purified water were added, and the resulting solution was further sufficiently stirred. After stirring, the solution was subjected to emulsification for 20 minutes with an ultrasonic homogenizer at 400  $\mu$ A. Thereafter, toluene was removed by heating under reduced pressure. Finally, the resulting emulsion was filtered through a filter having a pore size of 0.8  $\mu$ m, to give an aqueous dispersion of the dye-containing polymer particles.

[0064]

### Preparation Example 5

#### (1) Synthesis of Vinyl Polymer

Nitrogen gas replacement was sufficiently carried out in a 500-mL separable flask equipped with a dropping funnel and a Dimroth condenser. Thereafter, the flask was charged with 11 g of methacrylic chloride, 16 g of methyl methacrylate, 0.27 g of 2-mercaptoethanol and 10 g of 2-butanone, and the temperature of the ingredients was raised to 60°C under reflux. The dropping funnel was charged with 42 g of methacrylic chloride, 16 g of methyl methacrylate, 1.06 g of 2-mercaptoethanol, 1.06 g of 2,2'-azobis(2,4-dimethylvaleronitrile) and 40 g of 2-butanone, and the resulting mixture was added dropwise to the flask over a period of 3 hours. After the dropwise addition, the resulting mixture was aged for 2 hours, and 0.27 g of

2,2'-azobis(2,4-dimethylvaleronitrile) was added thereto. The resulting mixture was aged for additional 3 hours, and thereafter 75 g of stearylamine and 28 g of triethylamine were added thereto. The resulting mixture was aged for additional 3 hours. Thereafter, 150 g of 2-butanone was added thereto, and the resulting mixture was filtered through a membrane filter having a pore size of 3  $\mu\text{m}$ . All the solvent was once distilled off under reduced pressure, and 230 g of 1 N aqueous sodium hydroxide was added. The resulting solution was stirred for 3 hours, and filtered. The residue was washed three times with water, and the filtrate was filtered again and dried. 150 g of 2-butanone was added to dissolve the polymer. A solution of a vinyl polymer having a weight-average molecular weight of 7500 was thus obtained.

[0065]

(2) Aqueous Dispersion of Dye-Containing Polymer Particles

The amount 2.5 g of a yellow dye (commercially available from BASF, Neopen Yellow 075) was dissolved in 25 g of toluene. To the solution was added 5.0 g of the polymer solution obtained in the above (1), and the resulting solution was sufficiently stirred to dissolve the polymer. After the dissolution was confirmed, 1.45 g of 1 N aqueous potassium hydroxide and 125 g of purified water were added, and the resulting solution was further sufficiently stirred. After stirring, the solution was subjected to emulsification for 20 minutes with an ultrasonic homogenizer at 400  $\mu\text{A}$ . Thereafter, toluene was removed by heating under reduced pressure. Finally, the resulting emulsion was filtered through a filter having a pore size of 0.8  $\mu\text{m}$ , to give an aqueous dispersion of the dye-containing polymer particles.

[0066]

Comparative Preparation Example 1

The same procedures as in Preparation Example 1 were carried out except that tridecyl methacrylate in Preparation Example 1 was changed to dodecyl methacrylate, to give an aqueous dispersion of the dye-containing polymer particles.

[0067]

Comparative Preparation Example 2

The same procedures as in Preparation Example 3 were carried out except that tridecyl alcohol in Preparation Example 3 was changed to dodecyl alcohol, to give an aqueous dispersion of the dye-containing polymer particles.

[0068]

Comparative Preparation Example 3

The same procedures as in Preparation Example 5 were carried out except that stearylamine in Preparation Example 5 was changed to dodecylamine, to give an aqueous dispersion of the dye-containing polymer particles.

[0069]

Comparative Preparation Example 4

In the aqueous dispersion of the dye-containing polymer particles in Preparation Example 1, the same procedures as in Preparation Example 1 were carried out except that the amount of the magenta dye was changed to 1.5 g, the amount of the polymer solution was changed to 7.0 g, and the amount of 1 N aqueous potassium hydroxide was changed to 2.43 g, to give an aqueous dispersion of the dye-containing polymer particles.

[0070]

Examples 1 to 5 and Comparative Examples 1 to 4

There were mixed 8 parts by weight of the aqueous dispersion of the dye-containing polymer particles obtained in each of Preparation Examples 1 to 5 and Comparative Preparation Examples 1 to 4, 10 parts by weight of trimethylglycine, 5 parts by weight of urea, 5 parts by weight of triethylene glycol monobutyl ether, 1 part by weight of sodium 2-ethylhexylsulfosuccinate and 71 parts by weight of purified water. The resulting mixed solution was filtered through a 0.5  $\mu\text{m}$ -filter [acetylcellulose membrane, outside diameter: 2.5 cm, commercially available from Fuji Photo Film Co., Ltd.] placed in a 25-mL syringe [commercially available from TERUMO CORPORATION] without a needle, to remove coarse particles, thereby giving a water-based ink.

The water-based ink obtained in each Example is excellent in color tone and rubbing resistance.

[0071]

Next, the physical properties of the water-based inks obtained were evaluated in accordance with the following methods. The results are shown in Table 1.

[0072]

[Evaluation]

(1) Optical Density

The water-based ink composed of the above-mentioned components is filled in an ink cartridge BCI-21e for an inkjet printer commercially available from CANON INC., and the cartridge is set in the inkjet printer BJC-430J. Solid image printing is carried out on a common paper also usable for inkjet printing [commercially available from CANON INC., trade name: common paper also usable for inkjet printing PB Paper]. The printed paper is left in air at 25°C for

1 hour, and thereafter the optical density is measured by means of Macbeth densitometer RD914.

[0073]

(2) Printing Reliability

Two thousand sheets of a document in the test format are printed out on the above-mentioned paper using the above printer. The appearances of printed characters before and after the test are compared, and evaluated on the basis of the following evaluation criteria.

[Evaluation Criteria]

- : No clogging and no distortion are observed in printed characters.
- △: No clogging but slight distortion is observed in printed characters (problematic in practical use).
- ×: Generation of clogging is observed.

[0074]

Examples 6 to 10 and Comparative Examples 5 to 8

Water was added to 5 parts by weight of the solids contained in the aqueous dispersion of the dye-containing polymer particles obtained in each of Preparation Examples 1 to 5 and Comparative Preparation Examples 1 to 4 and 5 parts by weight of the permeability controlling solvent given below or 1 part by weight of the surfactant given below to make up to 100 parts by weight, to give a water-based ink. This water-based ink is placed in a bottle made of a fluororesin, and stored under an environment at 60°C for three months. Tests are conducted by the methods described below, and the ratio of retaining viscosity and average

particle diameter was calculated before and after the storage of the ink. The allowable range of the ratio of retaining viscosity and average particle diameter of the ink before and after the storage test is 90 to 110%, respectively.

[0075]

(Permeability Controlling Solvent)

Isopropanol, 2-Pyrrolidinone, Diethylene glycol monobutyl ether and Triethylene glycol monobutyl ether

(Surfactant)

Acetylenol EH [Kawaken Fine Chemical K.K., trade name]

[0076]

(1) Viscosity

The viscosity was determined at 20°C and 100 r/min using RE80L VISCOMETER (Rotor 1) commercially available from Toki Sangyo K.K.

[0077]

(2) Average Particle Diameter

The average particle diameter of the polymer particles containing a colorant, being contained in an ink (hereinafter referred to as the average particle diameter before storage) was determined using a laser particle analyzer system ELS-8000 commercially available from Otsuka Denshi K.K.

[0078]

(3) Ratio of Retaining Viscosity and Average Particle Diameter

The ratio of retaining viscosity and average particle diameter was determined by the equation:

[Ratio of Retaining Viscosity or Average Particle Diameter]

= ([Average Particle Diameter or Viscosity after Storage]/[Average Particle



Diameter or Viscosity before Storage))  $\times 100$

The results are shown in Tables 2 and 3.

[0079]

[Table 1]

Example No.	Optical Density	Printing Reliability
1	1.02	○
2	1.06	○
3	1.10	○
4	1.05	○
5	1.05	○
-----		
Comparative Example		
1	1.05	△
2	1.03	△
3	1.01	△
4	0.79	×

[0080]

[Table 2]

Example No.	Ratio of Retaining Viscosity (%)				
	Isopropanol	2-Pyrrolidinone	Diethylene Glycol Monobutyl Ether	Triethylene Glycol Monobutyl Ether	Acetylenol EH
6	99	101	102	108	102
7	98	103	104	100	100
8	105	98	99	107	104
9	96	99	100	97	99
10	102	104	102	103	103
Comp. Ex.					
5	125	124	126	136	123
6	129	120	125	120	129
7	132	133	128	130	128
8	89	98	97	87	99

[0081]

[Table 3]

Example No.	Ratio of Retaining Average Particle Diameter (%)				
	Isopropanol	2-Pyrrolidinone	Diethylene Glycol Monobutyl Ether	Triethylene Glycol Monobutyl Ether	Acetylenol EH
6	101	98	96	98	95
7	99	102	99	97	104
8	102	105	105	95	102
9	105	101	102	94	101
10	96	100	99	102	99
Comp. Ex.					
5	125	142	128	142	127
6	121	136	127	115	120
7	132	146	129	121	124
8	101	99	106	94	99

[0082]

It can be seen from the results shown in Tables 1 to 3 that the water-based ink obtained in each Example is excellent in storage stability and printing reliability, and exhibits high optical density.

[0083]

[Effects of the Invention]

The water-based ink of the present invention is excellent in storage stability and color tone, and exhibits high optical density and provides a printout having excellent rubbing resistance. In addition, the water-based ink of the present invention is excellent in printing reliability in addition to the above-mentioned properties when used for inkjet recording.

[Document] Abstract

[Abstract]

[Problems]

To provide a water-based ink which is excellent in storage stability and color tone, and exhibits high optical density and provides a printout having excellent rubbing resistance, and to provide a water-based ink which is excellent in printing reliability in addition to the above-mentioned properties when used for inkjet recording.

[Solving Means]

A water-based ink comprising an aqueous dispersion of polymer particles of a water-dispersible polymer having an alkyl group of at least 13 carbon atoms in its side chain, and a hydrophobic dye.

[Selected Drawings] None

## BACKGROUND INFORMATION OF APPLICANT

Identification Number	[000000918]
1.	
Date of Conversion	August 24, 1990
[Reason for Conversion]	New Registration
Address	14-10, 1-chome, Kayaba-cho, Nihonbashi, Chuo-ku, Tokyo
Name	Kao Corporation
2.	
Date of Conversion	April 18, 2003
[Reason for Conversion]	Change of Name Change of Address
Address	14-10, 1-chome, Kayaba-cho, Nihonbashi, Chuo-ku, Tokyo
Name	Kao Corporation